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THE EFFECT OF PRESYNTHESIZED POWDER ADDITIVES IN COMBINED SYNTHESIS AND SINTERING OF $SrZrO_3$ CERAMICS

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It is demonstrated that adding presynthesized powder to the initial $SrCO_3$ and ZrO_2 mixed in a stoichiometric ratio to produce $SrZrO_3$ and combining synthesis with sintering yields denser ceramics than without such additive. This is due to the decreased degree of nonequilibrium of the process of preform consolidation as a consequence of a certain increase in friction between the particles and a decreased probability of local compactions. The effect of increasing internal fraction at the bifurcation point is comparable to the effect of external disturbances and internal fluctuations (noises), which is responsible for the instability of results.

Refractories are usually produced from polyfractional mixtures consisting of a coarse-grained compactly sintered filler and a finely dispersed binder. To obtain a coarse-grained filler from complex oxides (spinels, mullite, zirconates, etc.), it is usually necessary to perform several technological operations involving several phases of high-temperature treatment. First, highly disperse powders of initial components are produced, then they are mixed, compressed as briquettes, and heat-treated for the synthesis of a complex oxide. Usually such briquette and large grains in it have substantial porosity. Therefore, the briquette is crushed, milled to a finely dispersed state, then a new briquette is compressed from the powder and fired to a high density. Next, the briquette is crushed and the coarse fraction is screened for the coarse-grained filler. The yield of the coarse fraction is around 50%. The content of the coarse fraction in a refractory material is approximately 70% and of the finely disperse fraction is 30%. A part of the fine fraction is again used in sintering briquettes for the coarse-grained filler.

This procedure makes the production of refractories from complex oxides expensive and inhibits their application. Accordingly, the simplification of technology and especially decreasing the number of high-temperature treatment stages is an important goal. A promising way for saving power is single-stage firing combining synthesis and sintering in one stage.

When a compressed preform made of a binary mixture of powder oxides taken in a stoichiometric ratio is heated to produce a complex oxide, for instance, a $MeO - ZrO_2$ mixture (Me is Ca, Sr, and Ba), pores are formed due to the Kirkendale and Frenkel' effects and the volume of the sample increases [1]. This creates conditions for local compaction, as a consequence of which a rather strong skeleton with cavities arises, which later prevents the formation of a compact article. [1]. This is of special practical interest in producing refractories from complex oxides.

When complex oxides are sintered simultaneously with the chemical reaction of their formation, in addition to the three main bifurcations [2], another bifurcation is added related to the volumetric variations ensuing from the chemical reaction. The chemical, reaction influences the evolution of the skeleton structure and raises the degree of nonequilibrium of diffusion mass transfer. This bifurcation actually acts as the first main bifurcation in sintering without a chemical reaction, when local compactions formed in molding and drying disappear and new ones emerge (an abrupt modification of the skeleton structure). As a consequence of self-organization, a skeleton arises consisting of compact areas, between which large pores exist, which cannot be removed at the final stages of sintering, accordingly, high-density ceramic cannot be obtained. This can be regarded as the accumulation of a part of excessive energy by the system for the formation of new surfaces (pores).

The multistability of the system with significantly different stable states is the reason for a low reproducibility of the ceramic structure [3]. Such low reproducibility can be eliminated using the internal or external control signals [2]. The role of internal control signals is usually played by structural elements created in ceramics at the preceding technological stages.

The difference in the diffusion coefficients of strontium and zirconium cations in the chemical reaction of $SrZrO_3$ formation leads to the formation of a hollow skeleton consisting of highly disperse sintering-active articles [1, 4]. The

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particles of the skeleton have many free surfaces, i.e., the excessive surface energy of the preform is very high. The system exists in the state of an unstable dynamic equilibrium, when it is impossible to predict its subsequent evolution. A specific feature of this state is enhanced sensitivity of the system to external effects and internal fluctuations [2]. This is responsible for certain specifics of controlling the compaction process. On the one hand, an effect can be rather small, on the other hand, it necessarily has to exceed the level of uncontrollable effects (noises) in order to reliably predict the further evolution of the system.

In order to successfully control the process, it is necessary to create the conditions where the system has sufficient time for dissipating energy by means of the more uniform compaction of the whole preform. Otherwise, the system is forced to accumulate part of energy for the formation of new surfaces, for instance, pores. A attempt was made to delay the process of the expansion of the preform during the formation of the hollow skeleton and its subsequent shrinkage. For this purpose a certain quantity of presynthesized strontium zirconate was added to the initial powdered mixture of oxides, to act as an inner control effect. Such additive acts as seeds of the new phase and shifts the beginning of the reaction of $SrZrO_3$ formation toward the lower temperature range. Furthermore, this filler increases the internal friction inside the preform deforming in sintering and thus impedes its expansion and shrinkage.

Materials for the synthesis of $SrZrO_3$ were $SrCO_3$ of grade "pure" and ZrO_2 of grade "analytically pure" taken in a stoichiometric ratio. Initially ZrO_2 powder was milled in a ball mill with ZrO_2 balls to a particle size below 5 μm, then $SrCO_3$ was added and mixed in joint dry milling. To the resulting mixture a certain quantity of $SrZrO_3$ powder previously synthesized from the same initial components with a particle size below 3 μm was added.

Samples shaped as bars of size $5 \times 5 \times 50$ mm were molded using a polyvinyl alcohol binder at a pressure of 100 MPa, fired in the air medium at a temperature of 1400 and 1650°C in a furnace with lanthanum chromite heaters for 2 h. After firing, the shrinkage of the samples was measured by hydrostatic weighing and their porosity and density were determined. The total porosity was determined taking the true density of $SrZrO_3$ equal to 5.48 g/cm^3 [1]. The ceramic microstructure was analyzed using an optical microscope.

The dependences of apparent density, open and total porosity, and shrinkage on the quantity of presynthesized $SrZrO_3$ additive are presented in Table 1. It can be seen that the shrinkage and density of samples at first grow perceptible with an increasing amount of additive and then start decreasing. The minimum total porosity and the maximum shrinkage and apparent density were registered in samples with additive content around 10%.[2] The open porosity constantly decreases with an increasing content of the additive.

[2] Here and elsewhere in wt.%.

TABLE 1

$SrZrO_3$ additive, %	Apparent density, g/cm^3	Open porosity, %	Linear shrinkage, %
Combined synthesis and sintering (1650°C, 2 h)			
0	4.40	11.60	7.4
5	4.57	4.10	9.3
10	4.65	3.10	10.2
15	4.49	2.50	9.0
20	4.42	0.02	8.8
30	4.30	0.00	10.2
Combined synthesis and sintering (1400°C, 2 h)			
0	3.96	22.0	3.8
5	3.85	23.8	4.2
10	4.03	20.3	5.4
15	4.46	9.8	8.3
20	4.71	4.2	9.9
30	3.69	3.7	8.5
Combined synthesis and sintering in drum No. 1 (1650°C, 2 h)			
0	4.08	25.4	15.4
5	4.71	14.0	18.1
15	4.94	8.1	17.4
30	5.00	5.1	16.2
100	5.31	0.2	11.9
Combined synthesis and sintering in drum No. 2 (1650°C, 2 h)			
0	4.08	25.4	15.4
5	4.10	25.1	14.0
15	4.32	21.0	13.9
30	4.94	7.0	14.3
100	5.31	0.2	11.9

Two lots of samples were prepared from mixtures of the same composition; mixing was performed in a planetary mill, but in different drums of slightly different sizes. Both lots of samples were fired together, but the results differ perceptibly (Table 1).

The study of the macrostructure indicates that a preform without additive has compact areas of size 1 – 2 mm between which pores of size up to 100 μm are located. The increasing shrinkage with additive content growing from 20 to 30% is presumably due to the fact that the increased quantity of presynthesized $SrZrO_3$ is accompanied by a decreased content of synthesized zirconate and, accordingly, an expansion of the preform and an increasing quantity of large sealed pores. This increases the shrinkage.

The introduction of presynthesized $SrZrO_3$ into a mixture of $SrCO_3$ and ZrO_2 makes it possible to increase the density of the preform combining synthesis and sintering in one stage. The greater the quantity of $SrZrO_3$ introduced, the greater the friction between the particles being synthesized and the lower the degree of nonequilibrium of the process. This is manifested in decreasing open porosity. The increase in the total porosity with $SrZrO_3$ content over 10% and the decrease in apparent density and linear shrinkage is related to the formation of large sealed pores.

An interesting result was obtained in the case of slow heating and exposure of compressed mixture of $SrCO_3$ and

ZrO_2 at a temperature of 1400°C. The mixtures was sintered to a high density. In repeating the experiment, the result was not fully reproduced, but the density of the samples was high. At the same time, the same mixture after sintering at 1650°C had a significantly lower density. Apparently, the high sintering activity of synthesized $SrZrO_3$ was channeled not to local compaction, but to a uniform shrinkage by decreasing the degree of nonequilibrium of the sintering process. At a higher sintering temperature this temperature range was passed quickly. As a consequence, the degree of nonequilibrium became higher, and the system had to accumulate part of energy for the formation of pores.

The incompletion of the process of synthesis increases local nonequilibrium and contributes to local compaction [4]. Under a slow heating rate the expansion of the preform made of the binary mixture of powder oxides before the end of the synthesis is slightly higher than in similar preforms heated faster, since in the latter case the expansion is partly compensated by the sintering of the synthesized phase. After firing the density of slowly heated samples was higher than that of rapidly heated ones. More intense local compaction in fast heating of a preform leads to lower shrinkage and density after the end of the firing.

The experiments indicate that although certain increase in the friction between particles raises the density of the preform after firing, results differ perceptibly from one experiment to another. This phenomenon was frequently encountered before in attempts to produce dense ceramics from strontium zirconate in combined synthesis and sintering. It used to be attributed to violations of the technology or to an insufficient knowledge of the process and, accordingly a failure to take into account some significant factors. The system in the unstable state acquires increased sensitivity to external disturbances and inner fluctuations (noises). An external control action, which is our case is increasing internal friction due to the introduction of presynthesized powder, should reliably exceed the level of these uncontrollable effects. In our case the level of these effects is comparable to the effect of the slightly increased friction between the particles. The control action turns out insufficient to uniquely determine the future evolution of the preform. Although the introduction of the additive increased the density of samples, they differed perceptibly in their properties.

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